Characterization of Esters of Fatty Acids and Dicarboxylic Acids with Guerbet Alcohols

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ABSTRACT: Esters of some common fatty acids and diacids with Guerbet alcohols were prepared by *p*-toluenesulfonic acid-catalyzed esterification. Such materials are of interest in applications such as additives in various industrial products. Gas chromatography–mass spectrometry with chemical ionization using methane as ionization gas is an efficient characterization method for these Guerbet esters and diesters. Under these conditions, structural features such as molecular weight and site of branching are easily determined. The spectra of the present compounds were compared to those of di-Guerbet esters reported earlier and differences noted. The compounds were also characterized by ^{13}C nuclear magnetic resonance spectroscopy.

Paper no. J9769 in *JAOCS 78,* 537–540 (May 2001).

KEY WORDS: Dicarboxylic acids, fatty acids, Guerbet alcohols, mass spectrometry, nuclear magnetic resonance spectroscopy.

The introduction of branched or bulky moieties into the structure of esters of various acids can enhance properties (for example, fluidity range) required for numerous practical applications such as lubricants and cosmetics (1–10). On the other hand, some compounds with bulky moieties did not significantly influence the cloud point of vegetable oil methyl esters (11), which would be required to improve the cold-flow properties of those esters when used as alternative diesel fuel (biodiesel).

While simple branched fatty esters derived from isopropanol or branched C_4-alcohols have been well-characterized, esters utilizing other branched alcohols have been synthesized and utilized, especially as reported in patent literature, but often their characterization has been lacking. Therefore, recently we characterized, especially by gas chromatography–mass spectrometry (GC–MS) with positive chemical ionization (PCI) and nuclear magnetic resonance (NMR), esters termed di-Guerbet esters (12), which are esters of a Guerbet acid (acids with an alkyl chain in the 2-position) with a Guerbet alcohol (alcohols with an alkyl chain in the 2-position; see Fig. 1 for a depiction of their structure), as well as other long-chain compounds with branched or bulky moieties (11).

The Guerbet reaction is summarily a dimerization of alcohols but actually is a modified aldol condensation with accompanying *in situ* dehydrogenation and hydrogenation steps (13). In the present paper, previous work (11,12) is extended to the Guerbet esters of mono- and di-acids whose structure is depicted in Figure 1. As in previous work (11), the background was to possibly develop additives that positively influence the cold-flow properties of biodiesel.

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EXPERIMENTAL POSITIONS

All GC–MS runs were conducted on a Hewlett-Packard (Palo Alto, CA) 5890 Series II Plus gas chromatograph (column: 30 m × 0.25 mm HP-5MS; Hewlett-Packard Co.) coupled to a Hewlett-Packard 5989B mass spectrometer. Purified compounds were analyzed by preparing samples in acetone or hexane. Electron ionization (EI) MS was performed at 70 eV and positive chemical ionization (PCI)–MS with methane as reagent gas at 230 eV, source temperature 200°C and source pressure 0.5 Torr. PCI spectra were background-subtracted. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra ($CDCl_3$ solutions) were obtained on a Bruker (Rheinstetten, Germany) ARX-400 spectrometer.

Methyl soyate (biodiesel) conforming to the provisional ASTM (American Society for Testing and Materials) standard for low-temperature studies was obtained from Ag Environmental Products (Lenexa, KS).

α-Branched alcohols (Guerbet alcohols) were obtained from Jarchem Industries, Inc. (Newark, NJ). Dicarboxylic acids and *p*-toluenesulfonic acid were purchased from Aldrich Chemical Co. (Milwaukee, WI). Fatty acids were acquired from Nu-Chek-Prep, Inc. (Elysian, MN). Toluene was obtained from Fisher Chemical (Fair Lawn, NJ). The synthesis consisted of mixing the starting materials, catalyst, and solvent and then following a procedure described in the literature (16,17). Work-up consisted of washing with water until neutral, drying with sodium sulfate, and subsequent removal of toluene. Nearly quantitative yields were achieved in all reactions according to GC–MS analyses (EI mode) at this stage. The products were purified by high-performance liquid chromatography using a system consisting of a Gilson (Middleton, WI) 305 pump, a Rainin (Varian Associates, Menlo Park, CA) Dynamax 60 Å preparative-scale (41.4 mm i.d.) silica column, a Kratos (now Perkin-Elmer Corp., Norwalk, CT) Spectroflow 757 absorbance detector, and a Waters (Milford, MA) R401 differential refractometer. The solvent system was 90:10 hexane/ethyl acetate at a flow rate of 25 mL min^{-1}. Fractions were collected manually by following the real-time plots of the detector signals. All products were clear liquids at room temperature. General structures of the products are depicted in Figure 1. Table 1 contains specific information on the products.

RESULTS AND DISCUSSION

Several esters derived from diacids (glutaric, dimethylglutaric, adipic, suberic, sebacic) as well as some fatty acids (palmitic, stearic, oleic) and Guerbet alcohols ("Jarcol I-12" = 2-butyl-1-octanol, "Jarcol I-16" = 2-hexyl-1-decanol) were synthesized. They were also tested as additives for improving the cold-flow properties of biodiesel (methyl soyate) in a fashion similar to

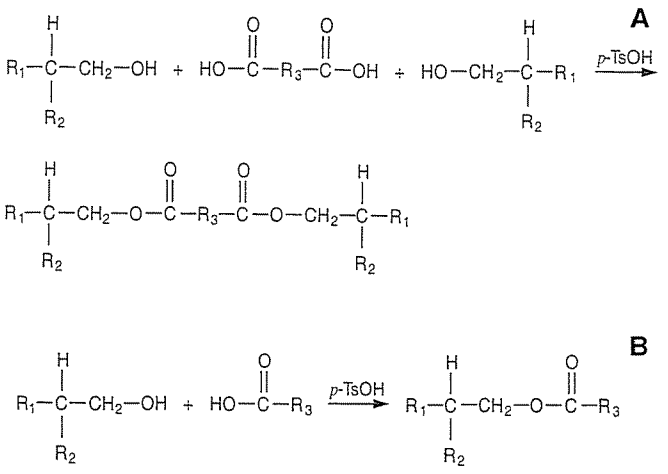

FIG. 1. Synthesis and structure of (A) Guerbet di-esters (R_1, R_2 = $-(CH_2)_nCH_3$; R_3 = $-(CH_2)_m-$), and (B) of Guerbet esters of fatty acids (R_1, R_2 = $-(CH_2)_nCH_3$; R_3 = $-(CH_2)_m-CH_3$ or $-(CH_2)_7-CH=CH-(CH_2)_7-CH_3$).

other potential additives with branched and bulky moieties (11). No significant improvements on the cold-flow properties of biodiesel were observed similar to that previous work on compounds with branched or bulky moieties, and no further results are reported here. Therefore, this paper focuses on the analytical characterization of the present compounds because, similar to di-Guerbet ester (12) and other compounds with branched and bulky moieties (11), little has been reported on this aspect despite an abundant body of mostly proprietary literature.

Similar to di-Guerbet ester (12) and other compounds with branched or bulky moieties (11), again GC–MS with PCI and methane as reagent gas is the most efficient method of unambiguously characterizing the present compounds. Similar observations were made in the characterization of esters of di- and tricarboxylic acids such as phthalates (14). A major reason for the suitability of CI–MS is that even with increasing molecular weight of esters, the spectra are less complex (compared to EI–MS) as was noted in early studies on CI–MS by Munson and Field (15). Another reason is that spectra obtained by means of methane CI also usually display strong molecular ions (15). In early studies on EI–MS of fatty esters, Ryhage and Stenhagen (16) noted that the esters of dibasic acids display only small molecular ions. Major mass spectral features of the two kinds of compounds studied here, Guerbet di-esters of diacids and Guerbet esters of fatty acids, will be discussed separately and then comparisons made between their spectra and those of previously discussed compounds (11,12).

Guerbet di-esters. The structure of Guerbet di-esters is depicted in Figure 1. PCI mass spectra of 2-butyloctyl-bis-glutarate and 2-butyloctyl-bis-octanedioate are depicted in Figures 2A,2B. The PCI mass spectrum of the Guerbet ester of a monoacid, 2-butyloctyl octadecanoate, is shown in Figure 2C. In the mass spectrum of 2-butyloctyl-bis-glutarate, major fragments arise as follows: *m/z* 133 is the protonated diacid ($[HO_2C–R–CO_2H + H]^+$), *m/z* 115 results from the loss of water from the protonated diacid, *m/z* 301 is the protonated monoacid monoester ($[R_1R_2CH–CH_2–O–CO–R_3–CO_2H + H]^+$) resulting from cleavage of one alcohol moiety, *m/z* 283 results from loss of water from the monoacid monoester to give an acylonium ion (general representation $[R–C\equiv O]^+$) (17), *m/z* 329 is the adduct of the monoester monoacid with $C_2H_5^+$ (18,19), and *m/z* 469 is the protonated molecular ion giving information on the molecular weight of the sample. The fragment *m/z* 169 is the alkyl part (R^+) of the alcohol moiety. In this connection, note that dodecanedioic and other diacids were shown to have an enhanced tendency to liberate water compared to their monobasic analogs (17). The protonation of species such as acids was demonstrated to arise through a McLafferty-type mechanism (20,21). The mass spectrum of 2-butyloctyl-bis-octanedioate displays the variation of the discussed peaks with the molecular weight (major fragments increased by 42 Da).

Guerbet esters of fatty acids. These esters display fragments similar to the Guerbet di-esters. In the PCI mass spectrum of 2-butyloctyl octadecanoate (Fig. 2C), the fragment at *m/z* 169 again corresponds to the alkyl rest of the Guerbet alcohol moiety, the fragment at *m/z* 285 is the protonated fatty acid, *m/z* 313 is the corresponding C_2H_5 adduct, and *m/z* 267 results from liberation of water of the protonated acid. In contrast to the esters of the diacids, here *m/z* 451 $[M - H]^+$ (which

TABLE 1
Compounds Synthesized in the Present Work

Starting materials	Product
Glutaric acid/2-butyl-1-octanol	2-Butyloctyl-bis-pentanedioate
Glutaric acid/2-hexyl-1-decanol	2-Hexyldecyl-bis-pentanedioate
2,2-Dimethylglutaric acid/2-butyl-1-octanol	2-Butyloctyl-bis-(2,2-dimethyl)pentanedioate
2,2-Dimethylglutaric acid/2-hexyl-1-decanol	2-Hexyldecyl-bis-(2,2-dimethyl)pentanedioate
Adipic acid/2-butyl-1-octanol	2-Butyloctyl-bis-hexanedioate
Adipic acid/2-hexyl-1-decanol	2-Hexyldecyl-bis-hexanedioate
Suberic acid/2-butyl-1-octanol	2-Butyloctyl-bis-octanedioate
Suberic acid/2-hexyl-1-decanol	2-Hexyldecyl-bis-octanedioate
Sebacic acid/2-hexyl-1-decanol	2-Hexyldecyl-bis-decanedioate
Palmitic acid/2-butyl-1-octanol	2-Butyloctyl-hexadecanoate
Palmitic acid/2-hexyl-1-decanol	2-Hexyldecyl-hexadecanoate
Stearic acid/2-butyl-1-octanol	2-Butyloctyl octadecanoate
Stearic acid/2-hexyl-1-decanol	2-Hexyldecyl-octadecanoate
Oleic acid/2-butyl-1-octanol	2-Butyloctyl-9(*Z*)-octadecenoate
Oleic acid/2-hexyl-1-decanol	2-Hexyldecyl-9(*Z*)-octadecenoate

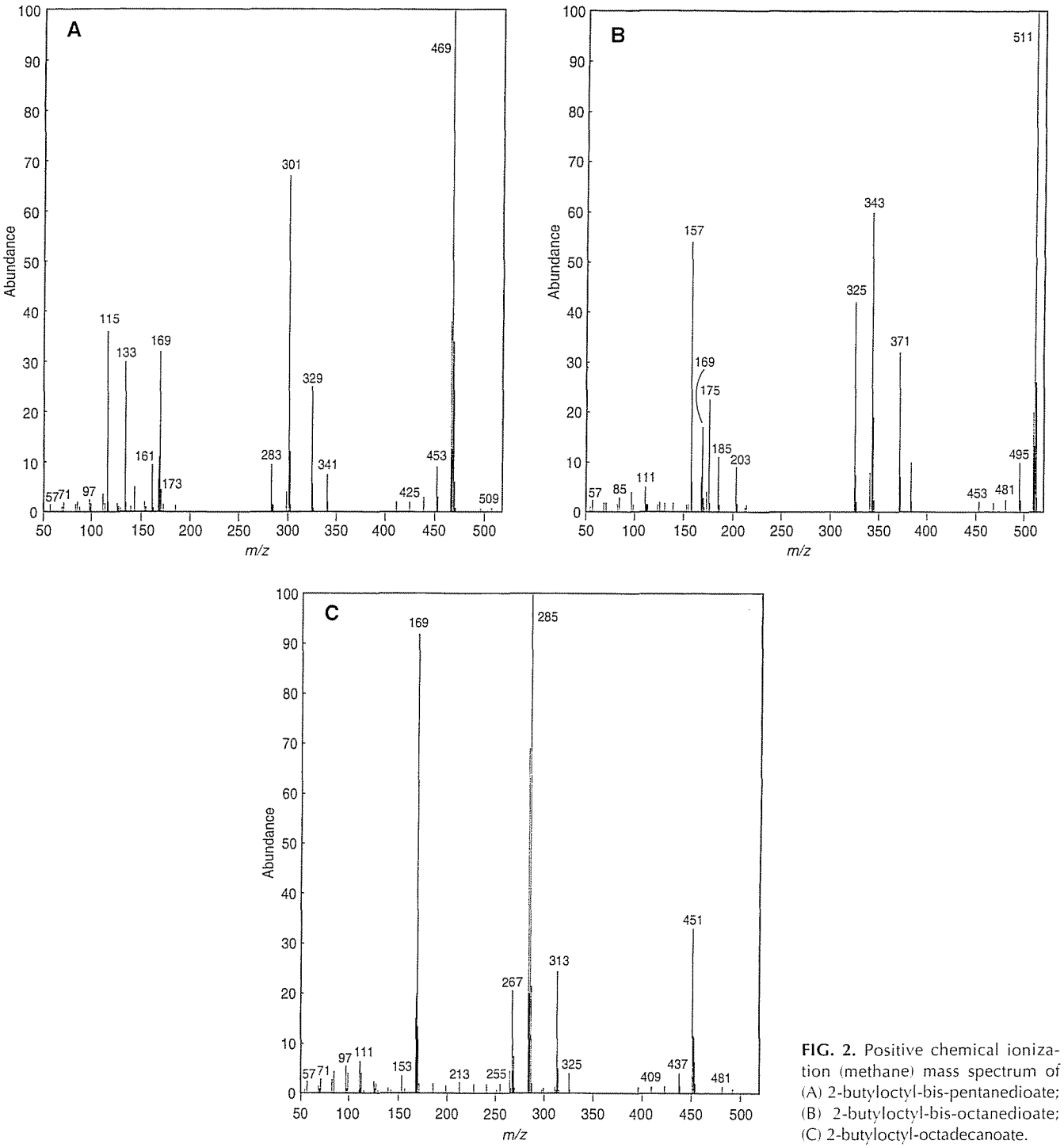

FIG. 2. Positive chemical ionization (methane) mass spectrum of (A) 2-butyloctyl-bis-pentanedioate; (B) 2-butyloctyl-bis-octanedioate; (C) 2-butyloctyl-octadecanoate.

may actually correspond to $[M + H - H_2]^+$, see Ref. 18) is the stronger ion.

Some major aspects of the fragmentation patterns of both kinds of compounds correspond to previous results (11,12). However, other features of the present methane-based PCI spectra deserve additional attention. The spectra in Figure 2 show that the present compounds can successively lose methylene groups as demonstrated by four small peaks corresponding to $[M - H - 14n]^+$ with $n = 1$ to 4. Similar observations hold for the major smaller fragments. Here also, successive liberation of methylene units can be observed. This leads to two series of methylene loss co-existing for *m/z* below the smaller fragment resulting from the two moieties acid or alcohol. The esters of the monoacids apparently consecutively lose CH_2 from the acid moiety (see Fig. 2C). This loss of CH_2 is not apparent for the diacids even in case of the fragment which has lost only one alcohol moiety (*m/z* 301 in Fig. 2A, *m/z* 343 in Fig. 2B).

The spectra of the present compounds lack all indications of McLafferty rearrangement ions. In the previous report on di-Guerbet esters (12), up to four McLafferty rearrangement

ions were observed. These McLafferty ions were observed at high *m/z*, although with relatively low abundances. Two pairs of McLafferty ions existed. From the *m/z* values of each of these pairs, the molecular weight of a di-Guerbet ester could be deduced even if a molecular ion were not present (12). In early mass spectrometric studies on esters branched in the 2-position of the acid, Ryhage and Stenhagen (22) had observed two McLafferty ions. It has been known since early studies on the MS of fatty acids and esters (20,23) that the abundance of McLafferty rearrangement ions decreases with increasing molecular weight of the alcohol moiety for straight-chain acid moieties if the larger mass of the McLafferty ions results from the alcohol and not the acid moiety. Compared to the present Guerbet esters of mono- and diacids, the di-Guerbet ester have one additional point of branching at the 2-position of the carboxylic acid moiety. The additional branching in the di-Guerbet ester apparently is responsible for the McLafferty ions. The present results show that electronic factors can facilitate the formation of McLafferty rearrangement ions. The electron-donating effect of alkyl groups in the acid moiety may contribute to the stability of the positively charged McLafferty ions.

Thus, PCI MS is a straightforward method for structural analysis of compounds such as the present one. With this analytical method, molecular weight of the compounds, molecular weight of the building blocks comprising the compounds, and the position of branching in the compounds can be determined.

^{13}C NMR. Generally, the NMR spectra of the present compounds correspond to those reported previously for the di-Guerbet ester (12). However, in ^{13}C NMR of the Guerbet esters of the diacids, the signal of C1 (the C attached to the ester moiety) of the alcohol moiety is observed at 67.1–67.2 ppm. This is a slight shift compared to di-Guerbet ester, in which the signals of C1 are in the range of 66.5–66.6 ppm (16; see corresponding typographical error in Fig. 4 of Ref. 12, which should also read 66.5–66.6). For the Guerbet esters of the fatty acids, the C1 carbon signal of the Guerbet alcohol moiety is observed at 66.7–67.0 ppm. The signal of C-2 in the Guerbet alcohol moiety is found at 37.2–37.3 ppm which corresponds to the di-Guerbet ester (12). The signal of C1 of the diacids can be found at 172.9–173.9 ppm depending on the chain length of the diacid. In the longer diacids (suberic, sebacic), the shift value is greater, 173.7–173.9. In the shorter diacids, the signal is shifted downfield. Thus, for the di-Guerbet ester of adipic acid Guerbet ester, the value is 173.3–173.5 and for glutaric acid it is 172.9–173.1. For the Guerbet esters of the straight-chain fatty acids oleic, stearic and palmitic it is 173.7–174.0 which coincides with the values of the longer-chain diacids. These values agree with ranges given in the literature (24) for related compounds. In di-Guerbet ester, the C1 of the fatty acid moiety exhibited its signal at 176.7–176.8 ppm. The ^{1}H NMR spectra generally are similar to those reported for di-Guerbet ester (12).

ACKNOWLEDGMENT

The author thanks Amanda L. Callison and Dale W. Ehmke for excellent technical assistance.

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[Received September 26, 2000; accepted February 26, 2001]